Wells.

An Analytical Study of the flue and Bag-house Dusts

from a Certain Smelting Plant

AN ANALYTICAL STUDY OF THE FLUE AND BAG-HOUSE
DUSTS FROM A CERTAIN SMELTING PLANT

BY

LANSING SADLER WELLS

A. B. University of Montana, 1915

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AN ANALYTICAL STUDY OF FLUE AND BAG-HOUSE DUSTS FROM A CERTAIN

SMELTING PLANT.

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AN ANALYTICAL STUDY OF FLUE AND BAG-HOUSE DUSTS FROM A CERTAIN SMELTING PLANT.

INTRODUCTION.

Purpose of the Investigation: Within the last few years the subject of "metallurgical smoke" has received a great deal of attention. The determination of its constituents is important for two reasons: many of these constituents are important commercially, and a large number are more or less poisonous to plant and animal life. A more thorough knowledge of the composition and means of recovery of the economic values of such smoke will tend to solve the problem of lessening or preventing its injurious action. It therefore seemed that an analytical study of the flue and bag-house dusts that go to make up part of "metallurgical smoke" might lead to some interesting results. The present investigation was carried out under the direction of Dr. George McPhail Smith, to whom the writer gratefully acknowledges his appreciation and indebtedness for his interest and advice.

An unbiased presentation of the problem of "metallurgical smoke" as it actually exists has been set forth by C. H. Fulton (1). The question of the injurious action of those constituents that escape into the atmosphere is as yet far from settled (2). This phase of the question will be taken up in this paper only to the extent of pointing out those substances that may be poisonous in varying degrees to plant and animal life.

II. MATERIALS AND METHODS OF EXPERIMENTATION.

The flue and bag-house dusts used in this analytical study were from a lead smelter (the American Smelting and Refining Company of East Helena, Montana). While the name "dust" may be used to include the solid particles of a "metallurgical smoke " as distinguished from the gases, a finer distinction of the different constituents of the flue system may be made. Fulton (1) says: "In taking samples of settled solids from different parts of the flue system, it is not possible to state that one material is flue dust and another material is fume, for in nearly all samples the flue dust and fume are mixed. A ready distinction can, however, be made by means of chemical analysis. The flue dust - - - consists of solid particles of the furnace charge which have been carried over into the flue system by the velocity of the gages. An invariable constituent of the furnace charge is silica or insoluble matter. A fume, on the other hand, consisting as it does of condensed metallic vapors, is essentially free from silica, so that practically a silica limit might be established to differentiate between flue dust and fume. A material above five percent silica could be termed 'flue dust' and material below that 'fume'". Thus "metallurgical smoke" may be said to be composed of flue dust, fume, and gases. This distinction will be adhered to in this paper, and the phrases "blast furnace flue dust" and "bag-house fume" will be used to distinguish these two constituents.

There are at present two methods employed to recover fume: filtration of the metallurgical smoke thru cotton or woolen bags (3), and the Cottrell (4) or electrical fume precipitation.

Nearly all lead smelters in this country use bag-houses for fume recovery. A bag-house is divided into as many compartments as there are flues leading into it. The smoke coming thru these flues is filtered thru cotton or woolen bags 18 inches in diameter and from 30 to 33 feet in length. These bags are suspended -from the supports at the ceiling of the building and the lower ends are fastened over flues at the bottom. Each bag-house has from 3,000 to 4,000 such bags. Woolen bags have been found to be more satisfactory than cotton ones. The smelter smoke that reaches the bag-house must fulfill two conditions: it must first be of a temperature low enough to prevent the schorching of the fabric of the bags, and it must be quite free from sulfuric acid that would finally corrode the bags. By cooling the smoke down to about 55 to 60 deg. C. these conditions will be met. However the temperature may often or usually run from 83 to 97 deg. C.

The blast furnace flue dust is composed of particles of the ore charge as mentioned above. It is dark gray to black in color and varies greatly in size, ranging from particles several millimetres in diameter to an extremely fine dust. In general it is similar in composition to the ore charge, only being finer. The samples used in this work were from a 20 pound bag, and a large representative sample was obtained by repeatedly quartering the entire sample. This sample was ground fine enough to pass thru a 200-mesh sieve. Air dried samples were used in all determinations.

The bag-house fume is dark gray to black in color, and is rather light in weight, and difficult to handle. It is so soot-like that an attempt to sieve it had to be abandoned, as the

fume clogged the openings of the sieve.

The general procedure adopted in this investigation was to first make a qualitative analysis of the materials. Knowing the composition, a specific method could be selected and worked out for the determination of each constituent which it was desired to estimate.

III. EXPERIMENTAL DATA.

1. Qualitative Analysis:(a) Qualitative Analysis of Blast Furnace Flue Dust:

About two grams of the finely ground dust were used in this analysis. Different reagents were tried in order to find the most satisfactory means of getting the material into solution. It was first treated with water and filtered, the filtrate giving a faintly acid reaction. Since the dust was only partly soluble in water it was not worth while to analyse the soluble portion separately.

The flue dust was best decomposed by first treating it with hydrochloric acid. In this treatment it was found that much of the sulfur present was in the form of sulfide sulfur or sulfite sulfur, which were largely evolved as hydrogen sulfide and sulfur dioxide. Nitric acid was then added to the mixture and the dust was further dissolved. Sometimes also a little bromine-water was added. A dark gray residue remained from this treatment. It was filtered hot and washed with hot water in order to insure the presence in the filtrate of all the lead chloride.

The Insoluble Residue: The dark color of the residue was found to be due to free carbon (fromthe coke in the blast furnace charge). The largest bulk of the residue was found to be silica. This was removed as silicon tetrafluoride with hydrofluoric and sulfuric

acids. The residue remaining from this treatment was analyzed and found to contain lead, silver (trace), antimony, aluminium, titanium (trace), and considerable carbon. These constituents were probably in the residue as lead sulfate, silver chloride, antimony pentoxide, aluminium sesquioxide, titanium dioxide, and free carbon.

The Acid Solution: The filtrate from the insoluble residue containing nitric acid was evaporated almost to dryness to expel the excess of free acid. In all cases the acid concentration was then regulated so that 5 cubic centimetres of 6-normal hydrochloric, sulfuric, or nitric acid were present in 100 cubic centimetres of the solution. This is the concentration recommended by A. A. Noyes (5). A solution thus prepared was of the proper acid concentration for a systematic qualitative analysis where the use of hydrogen sulfide makes possible a rather exact separation of the so-called "Hydrogen Sulfide Group".

The hydrogen sulfide group is divided into two subgroups, the copper and the tin group, and contains those metals whose sulfides are precipitated from an acid solution of the concentration recommended above by means of hydrogen sulfide gas. In this analysis the precipitate came down first yellow in color, then red, and finally it turned black. The copper and tin group sulfides were then separated by ammonium sulfide in which the tin group is soluble with the formation of sulfo-salts. The undissolved copper group sulfides were black.

Analysis of the Copper Group:

The sulfides of the copper group were boiled with dilute nitric acid. A black residue remained which might indicate the presence of mercuric sulfide, platinum sulfide, gold, aur-

ous sulfide, molybdenum sulfides (MoS_2 or MoS_3) or those sulfides that were more or less enclosed by the sulfur to give a black color,- for example lead or copper sulfides. An analysis of this residue showed the presence of lead alone.

To the filtrate from the nitric acid treatment concentrated sulfuric acid was added, and the solution evaporated to fumes. In this way the nitrates were converted into sulfates. On diluting this solution a heavy, finely divided, white precipitate appeared, indicating the presence of lead. This precipitate was filtered off and dissolved in ammonium acetate and the lead precipitated and confirmed as lead chromate.

The sulfuric acid solution from the procedure above was made alkaline with ammonium hydroxide. A small white flocculent precipitate was formed, indicating the presence of bismuth; the blue color of the solution indicated the presence of copper (as tetrammine copper sulfate, $[Cu(NH_3)_4]SO_4$). The solution was filtered and the precipitate treated with sodium stannite solution, which reduced the bismuth oxy-hydroxide to dark colored metallic bismuth.

A small portion of the blue solution suspected to contain copper was acidified with acetic acid and treated with potassium ferrocyanide solution, which gave the characteristic red precipitate of copper ferrocyanide.

To the remainder of the solution potassium cyanide was added until the blue color disappeared, and then hydrogen sulfide was passed into the solution. A yellow precipitate of cadmium sulfide was formed.

Analysis of the Tin group:

The sulfo-salts of the tin group were decomposed with

dilute hydrochloric acid which precipitated these metals as deep
yellow flocculent sulfides. Any antimony or tin sulfides of this
group were then dissolved with concentrated hydrochloric acid,
while sulfides of arsenic, platinum, or molybdenum, and metallic
gold, selenium, or tellurium would be only slightly soluble in
this acid, provided the temperature were kept below the boiling
point. Since a yellow residue was obtained at this point an an-
alysis was made for these insoluble constituents. The residue was
dissolved in hydrochloric acid by adding solid potassium chlor-
ate until the reaction was complete. On evaporating the solution
no yellow precipitate of potassium chloroplatinate was obtained,
showing the absence of platinum. The solution was then made al-
kaline with ammonium hydroxide and magnesium ammonium chloride
reagent was added. A heavy white crystalline precipitate was
formed indicating magnesium ammonium arsenate, $MgNH_4AsO_4$. This
precipiate was dissolved in dilute hydrochloric acid (Sp. Gr.
1.12) and hydrogen sulfide was passed into the hot solution. A
yellow precipitate showed the presence of arsenic. To the fil-
trate from the precipitate of magnesium ammonium arsenate sat-
urated oxalic acid solution was added and the excess of ammonia
was expelled by evaporation. Gold was found to be absent by this
test, since no purple precipitate of metallic gold was formed.
While oxalic acid is a sufficiently strong reducing agent to re-
duce most gold from salts to the free metallic state it will not
reduce selenium salts or acids. Using a stronger reducing agent,
as sulfurous acid, a small red precipitate of selenium appeared.
To the filtrate was added potassium iodide, which gave a small
black precipitate of tellurium tetra-iodide, TeI_4. No molybdenum
was found in the filtrate from the tellurium tetra-iodide; with

potassium thiocyanate molybdenum gives a red color that is not reduced by nascent hydrogen from zinc.

The solution of the sulfides obtained from the hydrochloric acid separation of antimony and tin from arsenic and the other insoluble sulfides was diluted somewhat and hydrogen sulfide again passed into it to precipitate any antimony sulfide. A small orange precipitate indicated the presence of antimony. No tin was found in the filtrate.

Analysis of the Ammonium Sulfide Group:

The filtrate from the hydrogen sulfide group was boiled to expel the hydrogen sulfide. On making this solution alkaline with ammonium hydroxide a green precipitate was formed, which was rapidly oxidized to a dark brown, indicating the presence of iron, and manganese. Hydrogen sulfide was then passed into the mixture and a black precipitate resulted. This color showed the possible presence of iron, cobalt or nickel; it would also mask the colors of any other precipitates. The filtrate from this precipitate was examined later for the ammonium carbonate and soluble groups after first testing it for the presence of vanadium. This was done by adding some more ammonium hydroxide and again saturating the solution with hydrogen sulfide. No characteristic pink or violet-red color appeared, as an indication of vanadium.

The precipitate of the sulfides and hydroxides of the ammonium sulfide group was dissolved in hydrochloric acid, and the chlorides then converted to nitrates by repeated evaporation with nitric acid. This solution was then made alkaline with sodium hydroxide. The hydroxides of the iron group including iron, manganese, cobalt, nickel, titanium, zirconium, thallic thallium and uranium are thus completely precipitated and do not dissolve

in a moderate excess, as in the case of the aluminium group. This latter group contains chromium, zinc, vanadium, and beryllium, and all of these are in solution, due to their amphoteric character, in the form of soluble aluminate, $NaAlO_2$, chromite, $NaCrO_2$, zincate, Na_2ZnO_2, vanadate, Na_3VO_4, beryllate, Na_2BeO_2. Thallous thallium also remains in solution as thallous hydroxide, $TlOH$. Sodium peroxide was then added to the mixture and then a little sodium carbonate, and the solution boiled. The hydroxides of the iron group were oxidized to the higher valences, and any thallium precipitated as thallic hydroxide, $Tl(OH)_3$. Any aluminium group would have remained in solution even though chromium was oxidized from chromite to chromate, and uranium to peruranate.

Analysis of the Aluminium Group:

The filtrate containing this group was made neutral with nitric acid, and then, after the addition of a little bicarbonate, was heated in a pressure-flask in a steam-bath. A white flocculent precipitate was formed indicating the possible presence of zinc carbonate, aluminium hydroxide, or basic beryllium carbonate. The filtrate was tested for chromium, uranium, and vanadium.

The above precipitate was dissolved in hydrochloric acid and then made alkaline with ammonium hydroxide. A white flocculent precipitate appeared, indicating the presence of aluminium or beryllium. It was dissolved in dilute hydrochloric acid, and the aluminium precipitated as aluminium chloride, $AlCl_3.6H_2O$, out of an ethereal solution upon passing into it a stream of hydrogen chloride gas. On making the filtrate alkaline with ammonium hydroxide, no beryllium hydroxide was precipitated.

The sodium bicarbonate filtrate was made acid with nitric acid. A colorless solution showed the absence of chromium. No

precipitate of uranyl ammonium phosphate, $UO_2NH_4PO_4$, was formed
on the addition of sodium phosphate. On staurating the solution
with hydrogen sulfide, no violet-red color appeared, as would
have been the case in the presence of vanadium.

Analysis of the Iron Group:

The sodium peroxide precipitate was dissolved in nitric
acid and hydrogen peroxide. The manganese was separated from the
other metals of this group by oxidizing the manganous nitrate to
hydrated manganese dioxide - a dark brown to black precipitate.
A further oxidation of this precipitate by means of lead dioxide
produced the characteristic pink color of permanganic acid.

Phosphates were tested for with ammonium molybdate rea-
gent, and found to be present in too small amounts to interfere
with any subsequent tests. The filtrate was then made alkaline
with ammonium hydroxide, and a dark red precipitate indicated
the presence of ferric hydroxide. Iron was confirmed by dissol-
ving a small amount of this precipitate in dilute hydrochloric
acid and then precipitating the dark blue ferri-ferrocyanide
from the cold solution. The rest of the precipitate was dissol-
ved in hydrochloric acid (Sp.Gr. 1.12) and the ferric chloride
extracted from the solution with ether. The aqueous layer was
taken to fumes with sulfuric acid, diluted, and on the addition
of 3 per cent hydrogen peroxide and di-sodium hydrogen phosphate,
an orange-yellow color showed the presence of titanium, and a floccu-
lent white precipitate that of zirconium. The titanium was
reduced with sulfurous acid, and the orange-yellow color disap-
peared, with the formation of a white precipitate of titanium
basic phosphate, $Ti(OH)PO_4$.

The first ether extract was tested for thallium with potassium iodide, but no yellow precipitate of thallous iodide appeared, after previous reduction with sulfurous acid.

The ammoniacal filtrate from the iron precipitate was saturated with hydrogen sulfide. The absence of a black precipitate proved that nickel and cobalt were not present in sufficient quantities to be detected by this method. A white precipitate indicated zinc, which was further examined and confirmed as zinc sulfide.

Analysis of the Ammonium Carbonate Group:

Ammonium carbonate and alcohol were added to the filtrate from the ammonium sulfide group, which gave a white precipitate indicating the presence of barium, strontium, calcium, and possibly magnesium.

The precipitate was dissolved in dilute acetic acid, and potassium dichromate was added to the solution. The absence of barium was shown by the failure to obtain a yellow precipitate. The dichromate solution was changed to the chromate with ammonium hydroxide, and then alcohol was added to this solution. Under these conditions strontium would have given a yellow precipitate of strontium chromate, but no precipitate came down.

To the solution ammonium oxalate was added, and this gave a heavy white precipitate of calcium oxalate. To the filtrate from this precipitate di-sodium hydrogen phosphate and about one-third the volume of ammonium hydroxide were added. A white crystalline precipitate of magnesium ammonium phosphate, $MgNH_4PO_4$, showed the presence of magnesium.

Analysis of the Alkali Group:

This group is the last or soluble group, and contains

the metals whose salts are not precipitated by the preceeding group-reagents. The filtrate from the ammonium carbonate group was evaporated, and ignited to remove ammonium salts. One-third of the solution was tested for potassium with chloroplatinic acid in an alcohol solution. A yellow precipitate of potassium chloroplatinate showed the presence of this metal, and it was further confirmed by the flame-test. The sodium was found by precipitating di-sodium di-hydrogen pyroantimoniate and also by the flame-test. Lithium was found to be absent, while rubidium and caesium were not tested for.

Detection of Non-metals:

Among the non-metallic constituents tested for and found to be present were:silicates and phosphates and free carbon (already mentioned), sulfide sulfur, sulfites, sulfates, and a small amount of chloride.

(b) Qualitative Analysis of Bag-House Fume:

The analysis of this material was carried out according to the procedure already described in the case of the blast-furnace flue dust. The fume was more completely soluble in hydrochloric and nitric acids, and left only a small residue.

The following table compiled from the qualitative analytical data of both the blast furnace flue dust and the baghouse fume shows in a comparative way the relation of the differ-constituents found in these materials.

TABLE I, QUALITATIVE ANALYSIS.

Constituents	Blast Furnace Dust	Bag-House Fume.
Insoluble residue from acid treatment	Fairly large amount. Dark gray color.	Small amount. Light gray color.
Silver	Trace	Trace
Lead	Large amount	Very large amount
Mercury	Absent	Absent
Bismuth	Trace	Trace
Copper	Small amount	Absent
Cadmium	Small amount	Fairly large amount
Arsenic	Fairly large amount	Large amount
Antimony	Trace	Small amount
Tin	Absent	Absent
Gold	Absent (by wet test)	Absent (by wet test)
Platinum	Absent	Absent
Selenium	Trace	Small amount
Tellurium	Trace	Trace
Molybdenum	Absent	Trace
Aluminium	Small amount	Small amount
Chromium	Absent	Absent
Vanadium	Absent	Absent
Uranium	Absent	Absent
Beryllium	Absent	Absent
Zinc	Fairly large amount	Small amount
Manganese	Small amount	Small amount
Iron	Large amount	Small amount
Titanium	Trace	Trace
Zirconium	Trace	Trace
Thallium	Absent	Trace

TABLE I (continued)

Constituents	Blast Furnace Dust	Bag-House Fume.
Nickel	Absent	Absent
Cobalt	Absent	Absent
Barium	Absent	Absent
Strontium	Absent	Absent
Calcium	Fairly large amount	Absent
Magnesium	Small amount	Absent
Potassium	Trace	Trace
Sodium	Small amount	Small amount
Lithium	Absent	Absent
Phosphate	Trace	Trace
Chloride	Small amount	Small amount
Sulfur		
(a) Sulfide	Small amount	Larger amount
(b) Sulfite	Small amount	Fairly large amount
(c) Sulfate	Large amount	Fairly large amount
Carbon(free)	Considerable	Small amount
Silica	Large amount	Small amount

2. QUANTITATIVE ANALYSIS:

The following table (II) contains the quantitative exper-
imental data which has been obtained in this investigation. The
results are expressed in percentages, and are the average of from
two to four determinations. All of the analyses were made on well-
bottled air-dried samples which were weighed from glass-stoppered
weighing-bottles. The different constituents are tabulated in the
form in which it was judged they might exist in the material.

TABLE II, QUANTITATIVE ANALYSIS.

Constituents	Blast Furnace Dust (per cent)	Bag-House Fume. (per cent)
Insol. $HCl + HNO_3$	11.12	0.61
Insol. $HCl + HNO_3 + NH_4C_2H_3O_2$	10.59	Not determined
Insoluble as $PbSO_4$	0.53	Not determined
Silica (SiO_2)	9.00	0.57
[+]Silver (ounces per ton)	18.8	2.3
PbO	27.27	58.79
Bi_2O_3	Trace	Trace
CuO	1.07	None
CdO	Small amount. Not determined.	4.98
As_2O_3	4.14	12.04
Sb_2O_3	Trace	0.49
[+]Gold (ounces per ton)	0.14	Trace
Se	Trace	Trace
Te	Trace	Trace
Mo	Absent	Trace
ZnO	6.42	1.35
Al_2O_3	1.54	0.78
Fe_2O_3	15.22	0.86
MnO	0.71	0.22
TiO_2	Trace	Trace
ZrO_2	Trace	Trace
Tl	Absent	Trace
CaO	4.71	Absent
MgO	0.78	Absent
$K_2O + Na_2O$	Not determined	Not determined

TABLE II (continued)

Constituents	Blast Furnace Dust	Bag-House Fume.
Sulfur	(per cent)	(per cent)
(a) Total	9.28	14.01
(b) Sulfate Sulfur	7.10	6.41
(c) Sulfide + Sulfite Sulfur	2.18	7.60
P_2O_5	Trace	Trace
Cl (chloride)	Small amount. Not determined.	Small amount. Not determined.
C (free)	Considerable. Not determined.	Small amount. Not determined.

+ Figures for gold and silver taken from an analysis supplied by
  the smelter.

(a) Analysis of Blast-Furnace Flue Dust:

The character of this material has already been referred to under the discussion of materials.

Determination of Insoluble Residue: This analysis was made for the purpose of finding the extent of the solubility of the material in the more common acids. About 0.5 gram of the dust was treated first with dilute hydrochloric acid, whereby most of the sulfide sulfur was expelled as hydrogen sulfide, and the sulfite sulfur as sulfur dioxide, with the simultaneous liberation, of course, of some free sulfur, in case both were present. Nitric acid was then added, and the dust further decomposed. In case any sulfur separated out a little potassium chlorate was added to oxidize it. The solution was evaporated to dryness, hydrochloric acid added to effect solution, and the process repeated. It was then warmed/with hydrochloric acid until the solution was complete as possible, the residue was filtered off, and thoroughly washed with hot water, then ignited and weighed. In order to determine the percentage of lead sulfate in the residue the same proceedure of decomposition was followed except that the residue was washed with hot ammonium acetate solution as well as with hot water. In this way the lead sulfate was dissolved and a lower percentage of insoluble residue was obtained.

Silica: The ordinary sodium carbonate fusion for the determination of silica had to be abandoned, as the risk of alloying the platinum crucible with lead from the dust was too great. It was found that an excellent fusion mixture of four parts of sodium carbonate to one part of sodium hydroxide decomposed the dust very well, and permitted the use of a nickel crucible. The cooled

mass obtained from this fusion was taken up in water and dilute hydrochloric acid, and evaporated twice to dryness. It was then taken up with dilute hydrochloric acid, the silica filtered off, thoroughly washed, ignited, and weighed.

Lead: Lead was determined by Alexander's, or the ammonium molybdate method modified by Low (6). The sample was decomposed with hydrochloric and nitric acids, and finally taken to fumes with sulfuric acid. The mixture was then diluted with water, cooled to about 18 deg. C., and the lead sulfate and insoluble residue filtered off. The lead sulfate was dissolved in a hot solution of sodium acetate, and titrated hot with ammonium molybdate solution that had previously been standardized against pure lead. Tannic acid was used as an indicator. When all of the lead has been precipitated by ammonium molybdate, then a very slight excess of this reagent will produce a yellow color with the tannic acid.

Copper: The so-called iodide method was used in this analysis. A solution of sodium thiosulfate was standardized against pure copper. The copper was dissolved in nitric acid, evaporated almost to dryness to remove the excess of acid, diluted, made alkaline with ammonium hydroxide, and finally acid with acetic acid. To this solution was added potassium iodide, and the iodine liberated was titrated with sodium thiosulfate, using a starch solution to determine the presence of free iodine. The dust to be analyzed was decomposed by acids, the lead removed as sulfate, and the copper precipitated as the sulfide with sodium thiosulfate in a solution faintly acid with sulfuric acid. This precipitate was filtered off, ignited to the oxide, dissolved in concentrated nitric acid and a little potassium chlorate, evaporated to dryness, made alkaline with ammonium hydroxide, then acid with ace-

tic acid, and the titration completed as in the standardization.[10]

Arsenic: The determination of arsenic by Pearce's method as modified by Low (6) is based on the fact that the arsenic may be precipitated from a neutral solution as silver arsenate, and the amount of silver determined by the Volhard method, by titrating with a standard ammonium thiocyanate solution . The dust was decomposed by fusing it with sodium carbonateand potassium nitrate. The melted mass was extracted with water and dissolved in nitric acid. To this solution was added silver nitrate and then ammonium hydroxide and sodium acetate until the free nitric acid was replaced by acetic acid. Under these conditions the arsenic was precipitated as silver arsenate. This precipitate was thoroughly washed to remove all soluble silver salts, dissolved in nitric acid and the silver nitrate formed titrated with standardized ammonium thiocyanate solution. Knowing the amount of silver in the silver arsenate, it is easy to calculate the quantity of arsenic present.

Zinc: The method used was that developed by Low (6). A solution containing zinc may be titrated with potassium ferrocyanide, using uranyl acetate or nitrate as an outside indicator to determine the point at which all of the zinc has been precipitated by the potassium ferrocyanide. Pure zinc was used to standardize the potassium ferrocyanide solution. Since this dust was found to contain cadmium, a modification, as advised by Low, to aviod the high results from the presence of this metal, was used; but it was also modified somewhat to meet the requirements of this analysis. The principle of this modification is the use of potassium cyandie to dissolve zinc sulfide from cadmium sulfide. The analysis was carried out as follows: The dust was dissolved

first in hydrochloric acid, then nitric acid, and most of the arsenic expelled by the use of bromine , since arsenic bromide is quite volatile. The mixture was then taken to fumes with sulfuric acid, diluted, and ammonium chloride and ammonium hydroxide added. Manganese was then precipitated as manganese dioxide with bromine water, and the solution filtered. To the filtrate was added ammonium hydroxide until slightly alkaline, and then enough ammonium sulfide to precipitate the cadmium, lead, zinc, etc. The sulfides were filtered off, and then treated with potassium cyanide, which dissolved the zinc and copper sulfides but not the lead and cadmium sulfides. The filtrate was then made acid and the hydrocyanic acid expelled. This solution was then made alkaline with ammonium hydroxide, next slightly acid with hydrochloric acid, and any copper present precipitated with hydrogen sulfide, as cupric sulfide, CuS. The filtrate was then titrated with standardized potassium ferrocyanide solution.

Manganese: Manganese was determined by the Volhard (7) method. Manganese salts may be titrated in a neutral solution with potassium permanganate in the presence of zinc salts, to precipitate the tetravalent manganese formed as zinc manganite. The dust was dissolved in acids, made neutral, and a slight excess of zinc oxide was added. The solution was titrated hot with a standardized potasssium permanganate solution to a pink end-point.

Iron: The iron was determined by the method of Zimmermann-Reinhardt, as outlined by Treadwell (8). The potassium permanganate solution was standardized against pure iron wire. The pure iron wire was dissolved in hydrochloric acid, reduced with stannous chloride in the usual manner, some Zimmermann-Reinhardt preventative solution (amixture of manganous sulfate, sulfuric and phos-

phoric acids) added, and then titrated. After standardizing the
permanganate solution in this manner, the iron in the flue dust
was determined. The dust was dissolved in acids, filtered, and the
"hydrogen sulfide" metals precipitated with hydrogen sulfide in
acid solution. The iron was then precipitated as the hydroxide
with ammonium hydroxide, and this precipitate was dissolved in
hydrochloric acid. This solution was reduced with stannous chlor-
ide in the usual way, and titrated with potassium permanganate as
described above.

Aluminium: The hydroxides of aluminium and iron were precipitated
together, ignited and weighed. The iron was determined separately
by the permanganate titration, and its equivalent amount of fer-
ric oxide, Fe_2O_3, was subtracted from the total oxides; the dif-
ference was assumed to consist entirely of aluminium oxide, Al_2O_3
a somewhat questionable assumption.

Calcium: The calcium was precipitated with ammonium oxalate as
calcium oxalate, filtered, and washed with hot water. The pre-
cipitate was dissolved in warm dilute sulfuric acid, diluted
with hot water to 400 cubic centimetres, and titrated hot with
standardized potassium permanganate.

Magnesium: The filtrate from the calcium oxalate was neutralized
with hydrochloric acid, and the magnesium precipitated as the
phosphate as recommended by Gibbs. In this case the magnesium
was precipitated with a solution of microcosmic salt, $NaNH_4HPO_4$.
H_2O, when most of the magnesium present was at once thrown down
as amorphous magnesium hydrogen phosphate, $MgHPO_4$. Then about
one-third of the volume of 10 per cent ammonium hydroxide was
added, whereby the amorphous precipitate was transformed into
crystalline magnesium ammonium phosphate, $MgNH_4PO_4$. This precipi-

tate was filtered off, ignited, and weighed as magnesium pyro-phosphate, $Mg_2P_2O_7$.

Sulfur: Total sulfur: The dust was treated with bromine water, and with nitric and hydrochloric acids. The solution was then evaporated to dryness, and the residue dissolved in dilute hydro-chloric acid. This was evaporated, and the residue again taken up in dilute hydrochloric acid. The solution was then made alka-line with ammonium hydroxide, and a saturated solution of ammon-ium carbonate was added to convert any lead sulfate to the car-bonate, and render any combined sulfur trioxide soluble, as ammonium sulfate. The iron was then precipitated as the hydroxide and the solution filtered. The filtrate was neutralized, diluted to 400 cubic centimetres, and one cubic centimetre of hydrochlor-ic acid (Sp.Gr. 1.12) was added. This solution was heated nearly to boiling and 100 cubic centimetres of N/10 barium chloride solution (which was also hot) was added at once. The resulting mixture was heated to boiling, cooled, filtered through a Gooch filter, dried and weighed as barium sulfate, and from this the total amount of sulfur was calculated.

Sulfate in the presence of soluble sulfides: This determination was carried out as recommended by Treadwell (8). The weighed dust was placed in a flask, the air expelled by carbon dioxide, dilute hydrochloric acid added, and the solution boiled while carbon dioxide was passed through it until all of the sulfide had been expelled. The sulfuric acid was then precipitated from the solu-tion in the same manner as the total sulfur was determined above. This gave the percentage of sulfate sulfur/in the presence of soluble sulfide sulfur. The difference between this and the total

sulfur represents the amount of sulfur present as sulfide sulfur.

(b) Analysis of Bag-House Fume:

       The analysis of this material was carried out in the same way as that of the blast furnace flue dust just described. Those few constituents that were not determined in the case of the blast furnace dust require some discussion here.

Cadmium: Cadmium was determined as cadmium sulfate, as recomended by Treadwell ($\S$). The fume was dissolved in hydrochloric and nitric acids, and then taken to fumes with sulfuric acid; in this way most of the lead was precipitated as the sulfate. The filtrate which contained about 5 cubic centimetres of concentrated sulfuric acid was diluted to 100 cubic centimetres and hydrogen sulfide was passed into the solution. The sulfides of the tin group were dissolved from those of the copper group with ammonium polysulfide. The cadmium sulfide which remained undissolved in the ammonium polysulfide was dissolved in hot dilute hydrochloric acid, taken to fumes with sulfuric acid, the solution made up to the acid concentration as recommended above, and the cadmium precipitated again as the sulfide. This precipitate was then filtered, dissolved in dilute hydrochloric acid, converted into the sulfate with sulfuric acid, the free sulfuric acid evaporated, and the cadmium weighed as the sulfate.

Antimony: The principle of this determination was to to oxidize antimony from antimonous acid to antimonic acid with a standardized potassium permanganate solution. The fume was fused in a nickel crucible with a mixture of sodium peroxide and sodium hydroxide. The melted mass was cooled, extracted with water, and hydrochloric acid added. The solution was made up to the proper acid concentration and the sulfides of the hydrogen sulfide

group precipitated with that reagent. The solution was filtered,
and the copper and tin division sulfides separated with a solution
of ammonium and sodium sulfides, in which the tin division sul-
fides dissolve forming sulfo-salts. The filtrate containing these
sulfo-salts was made acid with dilute hydrochloric acid which
decomposed them, the sulfides of the tin division being precipi-
tated. The arsenic was separated from the antimony by the use of
concentrated hydrochloric acid in which antimony sulfide is solu-
ble. The residue of arsenic sulfide was then treated with sodium
carbonate solution in order to remove (by dissolving) the arsenic
sulfide from entrained sulfides of antimony. The residue of anti-
mony sulfide left after this treatment was dissolved in concen-
trated hydrochloric acid and the filtrate (from separated sulfur)
united to the one above. The antimony was again precipitated as
the sulfide with hydrogen sulfide and filtered. The precipitated
antimony sulfide was then dissolved in ammonium sulfide and to
this solution potassium acid sulfate and sulfuric acid were added.
The solution was then boiled to expel the free sulfuric acid,
allowed to cool, and the partially solidified residue was taken
up with 10 cubic centimetres of dilute hydrochloric acid, and
made up to a final volume of about 200 cubic centimetres. The
solution was then titrated with a potassium permanganate solution
that had been previously standardized against pure iron wire.

IV. Discussion of Results:

From a comparison of both the qualitative and quantita-
tive analyses, it will be noted that the bag-house fume contains
a larger percentage of the more volatile metals than the blast
furnace flue dust; especially is this true in the case of lead
and cadmium. In the case of sulfur, the differentiation between

the more volatile forms (sulfite and sulfide) and less volatile
forms (sulfate) is more marked, and still more so in the case of
arsenic. A comparison of the percentages of these more and less
volatile forms of sulfur will clearly indicate the retention of
the latter in the flues from the blast furnace, and of the former
in the bag-house, to which they have passed on as fume. This is a
condition to be desired as sulfur trioxide exerts a corrosive
action on the bags. The relatively high per cent of cadmium in
bag-house fume, and that of zinc in the blast furnace flue dust
is worthy of note.

These results have been reported as the percentages of
metallic oxides, in conformance with the usual proceedure, but,
as the components of the mixtures analyzed were formed largely
in a reducing atmosphere.(as is apparently indicated by the anal-
ysis) the advisability of so reporting them seems questionable;
it might have been preferable to report them either as sulfides
or as the free elements for the above reason.

Since the metallurgical smoke is cooled down to at
least 97 deg. Centigrade, and its speed lessened we should expect
to find the more volatile constituents settling out and being
filtered out in the bag-house; the analysis confirms this.

V. CONCLUSIONS:

The bag-house evidently retains much sulfite sulfur
and arsenic, admittedly injurious to plant and animal life if
present in sufficient amount. The figures indicate the retention
of a considerable quantity of both these constiuents, but as there
were available no data concerning the composition and amount of
the original furnace charge and of the composition, volume and
velocity of the gases discharged into the air, no conclusions can

be drawn as to how much this injurious effect is reduced by the
bag-house filtration.

It appears very probable that the bag-house fume could
well be applied as a source of cadmium, and , if larger quanti-
ties were worked up, some of the rarer elements (e. g., gallium,
indium, thallium, germanium) as well. Time did not permit the
working out of this most interesting phase of the problem.

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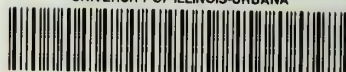   Smelter Fumes in the Atmosphere of Salt Lake
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